STINGER GHAFFARIAN TECHNOLOGIES

Application of ASTM E-1559 apparatus to study H_2O desorption

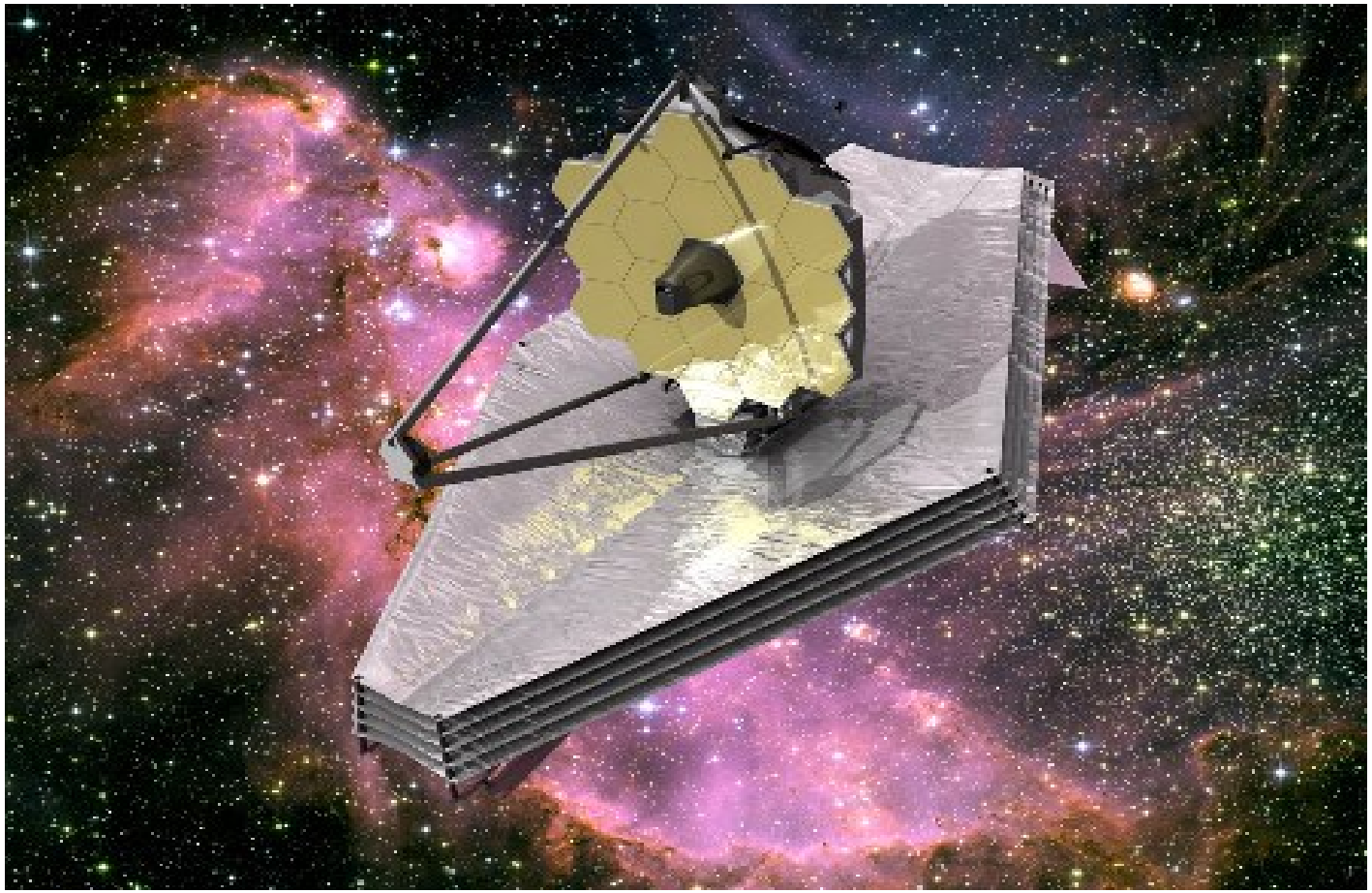
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2015 CONTAMINATION, COATINGS, MATERIALS, AND PLANETARY PROTECTION WORKSHOP
NASA GODDARD SPACE FLIGHT CENTER
29-31 JULY 2015

Outline

- Introduction
- Objectives
- Math model development
 - Clausius-Clayperon
 - Quantum Statistical Mechanics
- Selected candidate expressions
- ASTM E-1559 apparatus “MOLEKIT”
 - Physical description
 - Outgassing measurement procedure
 - Adaptation to desorption measurements
- Results & Discussion
- Concluding Remarks

JWST Observatory

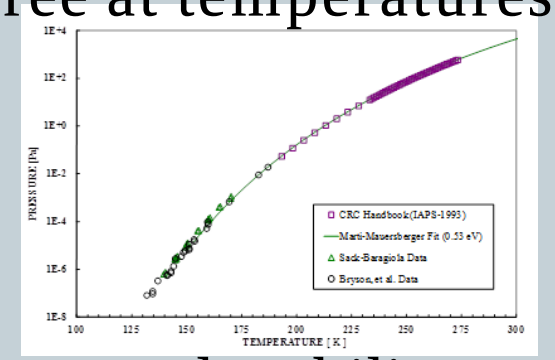


Introduction (2 of 3)

- James Webb Space Telescope (JWST)
 - Designed to operate for five years at L2
 - Contains four IR instruments operating below 50 K
 - Sunshield must reject nearly all solar input
 - Radiative properties extremely sensitive to water vapor deposits
- Electronics compartment on shadowed side will outgas more than enough water vapor to ruin sunshield effectiveness
 - Design vent to also collect sufficient fraction of water vapor
 - Account for temperature-dependent desorption of condensed material

Introduction (3 of 3)

- Noted $p_{v,H2O}$ models tended to disagree at temperatures in range of interest (120—140 K)
 - Typically based on data above 150 K
 - None found using data below 131 K
 - What model to use?



- Researchers cited limits for thermal control stability
- Our group has experience with ASTM E-1559 apparatus used to collect volatile outgassing rates down to liquid nitrogen temperatures (~90 K)
 - Can measure source rates of picograms/s
 - Very stable thermal conditions
- Simple matter to adapt to H_2O desorption study at cryogenic temperatures

Objectives

- Review formulation of water vapor desorption models
 - Features of high-fidelity physical expressions
 - Selected candidates
- Discuss use of NASA-GSFC outgassing measurement apparatus
 - “MOLEKIT” = “Molecular Kinetics”, ASTM E-1559 system
 - Sketch of operational procedures
 - Adaptation to desorption measurements

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Clausius-Clayperon

- Thermodynamically, equilibrium condition for single species in multiple phases characterized by minimum value for Gibbs free energy *G*
 - Obtained when *G* per mole is equal for each phase
 - Consequence of this condition gives *p* as function of *T*

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{l}{T\Delta v} = \frac{pl}{RT^2}$$

- For constant heat of transformation *l*, obtain Arrhenius-type expression

$$p_v(T) = p_{\text{ref}} \exp\left(\frac{-l}{RT}\right) = \exp\left(C - \frac{\Theta}{T}\right)$$

Quantum Statistical Mechanics

- On molecular scale, work with chemical potential μ, like Gibbs free energy per molecule
 - Determine chemical potentials for solid and gas are equal
- Molecular ensemble described by number of energy states available to phases, increases with T
 - Somewhat convoluted path for solid phase *1*, easier to describe gas phase *2* (monatomic)

$$\mu_1(T) = -\eta - T\int_0^T \frac{dT}{T'^2}\int_0^{T'} c(T'')dT'' \qquad \mu_2 = -kT\ln\left[\frac{kT}{p_2}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]$$

$$p_2(T) = \exp\left\{\ln\left[\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\right] + \frac{5}{2}\ln(T) - \frac{\eta}{kT} - \int_0^T \frac{dT}{kT'^2}\int_0^{T'} c(T'')dT''\right\}.$$

Quantum Stat. Mech.—Diatomic Gas

- For a diatomic gas, must incorporate influence of internal degrees of freedom (rotational+vibrational)

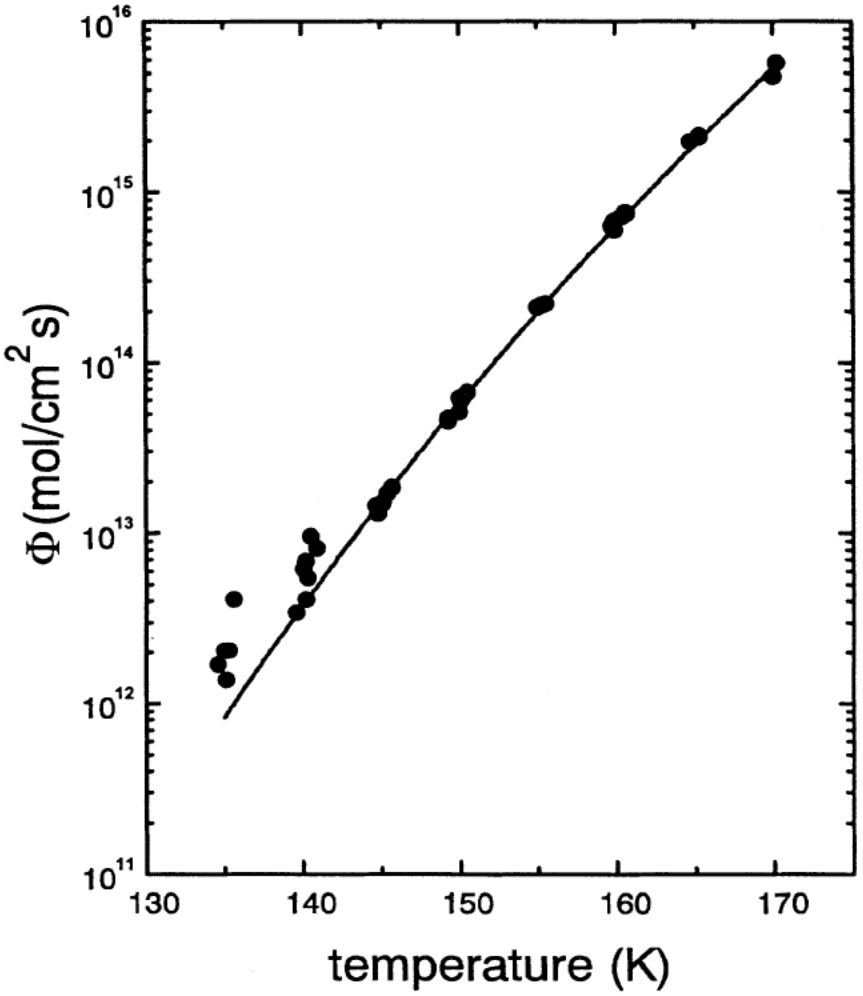
$$\mu_{2,\,\text{diatomic}} \approx -kT \ln\left[\frac{kT}{p_2}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\frac{I_{\text{rot}}kT}{\hbar^2}\exp\left(-\frac{\hbar\omega}{2kT}\right)\right]$$

$$p_{2,\,\text{diatomic}}(T) \approx \exp\left\{\ln\left[\frac{I_{\text{rot}}k^{\frac{7}{2}}}{\hbar^5}\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}\right]+\frac{7}{2}\ln(T)-\frac{(\eta+\hbar\omega/2)}{kT}-\int_0^T\frac{dT}{kT'^2}\int_0^{T'}c(T'')dT''\right\}$$

 - Notice heat of transformation term becomes modified!
- Water vapor is polyatomic, approximate internal d.f. physical models become increasingly approximate
 - Punt—replace terms in exponential with fit parameters, functions of temperature

Sack-Baragiola Observations

- Sack & Baragiola managed to produce sublimation data down to 135 K
 - Very careful to distinguish between different types of solid phase ice
 - Hexagonal crystalline
 - Cubic crystalline
 - Amorphous
- Noted that vapor deposited at low temperatures not necessarily in most equilibrium state, will relax with time, temp. dep.



Sack-Baragiola Formula

- Sack & Baragiola recommended the following formula for "stable crystalline" phase ice based on stat. mech. arguments:

$$p_{v,\text{S-B}} = BT^4 \exp\left(-E/kT\right) = \exp\left[\ln B + 4\ln\left(T\right) - \frac{E}{kT}\right]$$

 - $(B,E) = (29.3\ \text{Pa/K}^4, 10.375\ \text{kcal/mole})$
 - E identified as heat of sublimation = 0.45 ± 0.03 eV
 - Amorphous phase vapor pressure identified as being 100x higher
 - Review of paper indicates this rate should be less than 30x higher

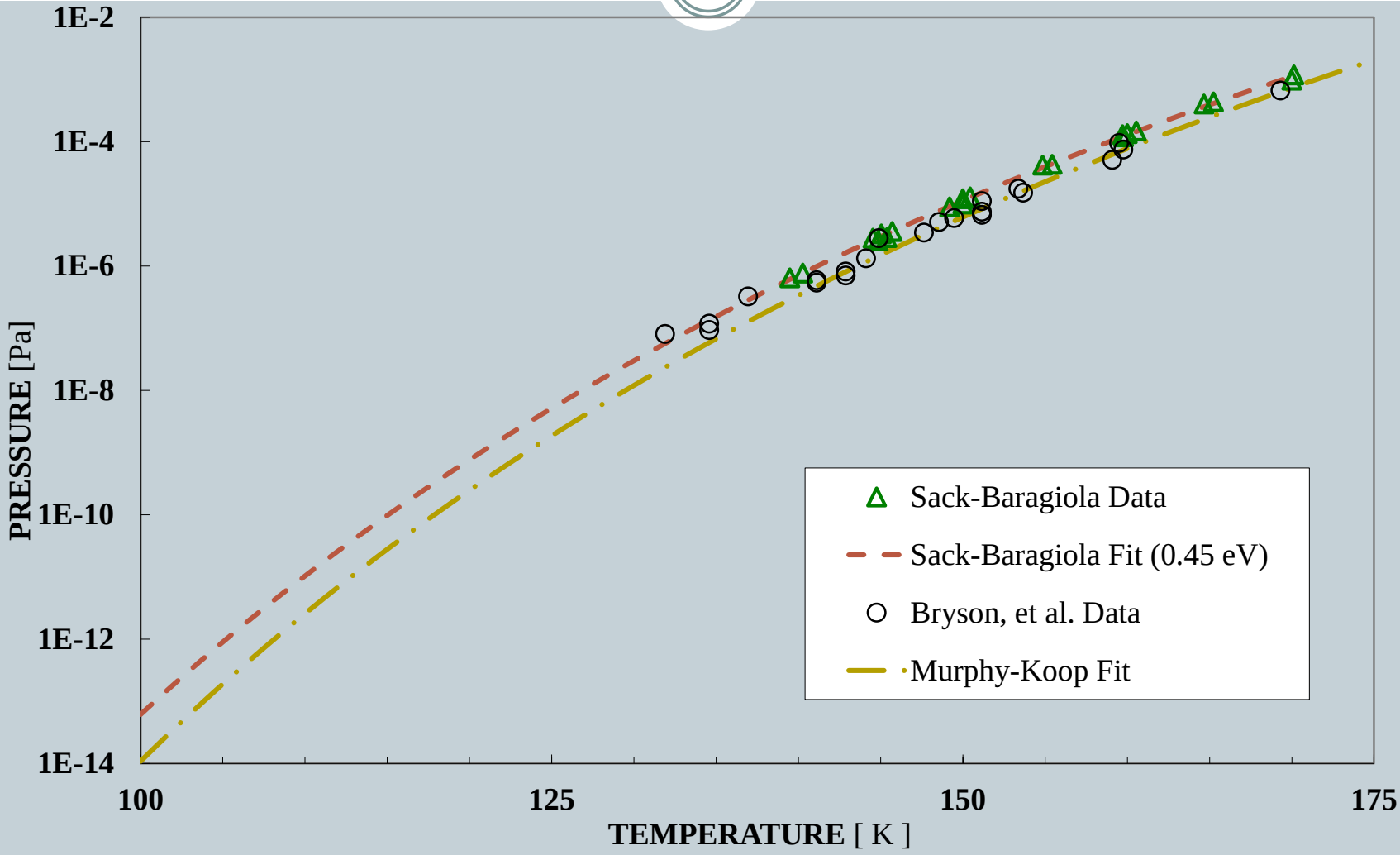
Murphy-Koop Formula

- Murphy & Koop discussed review of various authors, devised vapor pressure fit claiming use of Clausius-Clayperon equation, but accounting for temperature dependent behavior:

$$p_{v,\,\text{M-K}}\,[\text{Pa}] = \exp\left[9.550426 + 3.53068\ln(T) - \frac{5723.265}{T} - 0.00728332\,T\right]$$

 - based on
 - Solid phase ice specific heat data down to 110 K
 - Non-ideal gas behavior
 - Did M-K actually resort to stat. mech. arguments?
 - Not directly based on vapor pressure data

Model Comparison



Outline

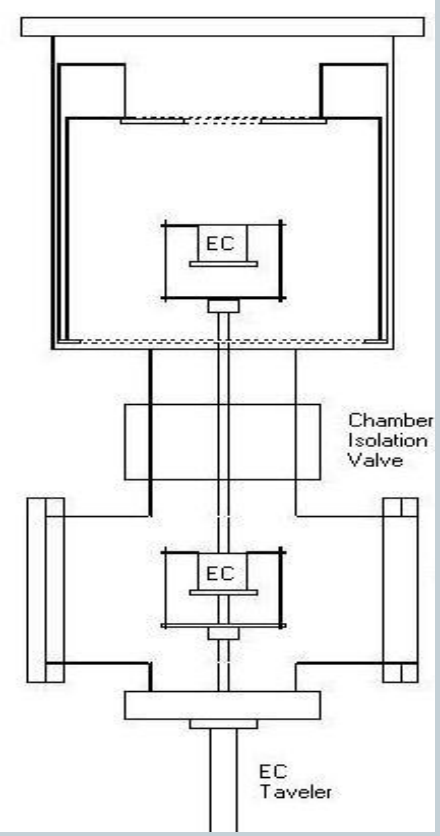
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Rationale

- Found very little $p_{v,\ H2O}$ data below 150 K, none below 131 K
- Description of Sack-Baragiola apparatus mentioned sensitivity level of 5.0e-4 molecular monolayers/s
 - May translate to a QCM sensitivity exceeding 10 Hz/hr
- Test times typically limited to < 15 min
 - Certain runs lasted ~ 3 hrs.
- NASA GSFC possesses an ASTM E-1559 apparatus designed to measure outgassing from sample materials for gases condensable as low as LN_2 would allow
- Often exhibits measurement stability within 0.1 Hz/hr over days-long periods
 - Could we measure vapor pressure levels two OOM below others?

MOLEKIT Description (Genl.)

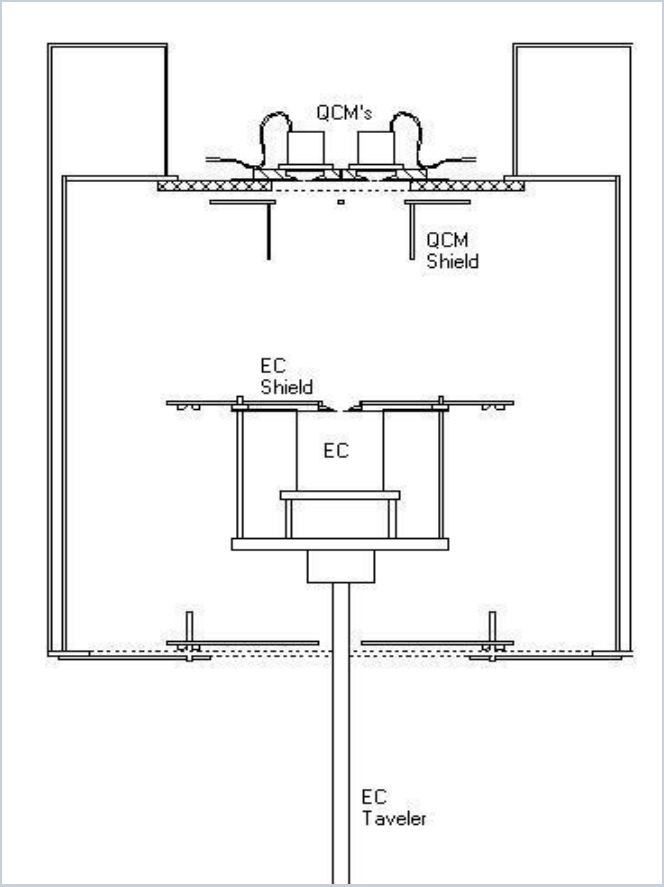
- Two vacuum chambers
 - Test chamber
 - Loading chamber
- Sample of test material inserted into Effusion Cell
 - Temperature controlled
 - Sample limited to < 2” cube
- Heated, translated from loading chamber into test chamber



MSW

MOLEKIT Description (Test Chamber)

- $(d, L) \approx (36”, 46”)$
- LN_2 cooled walls
- Four QCM’s
 - Cryogenically cooled (CQCM’s)
 - Temperatures individually controlled
 - Fixed, known viewfactors to EC
 - Can relate QCM collection rate to source outgassing rate (translate from Hz/hr to $g/cm^2/s$)
- Under equilibrium, $p_v = \dot{\phi}\sqrt{2\pi RT}$



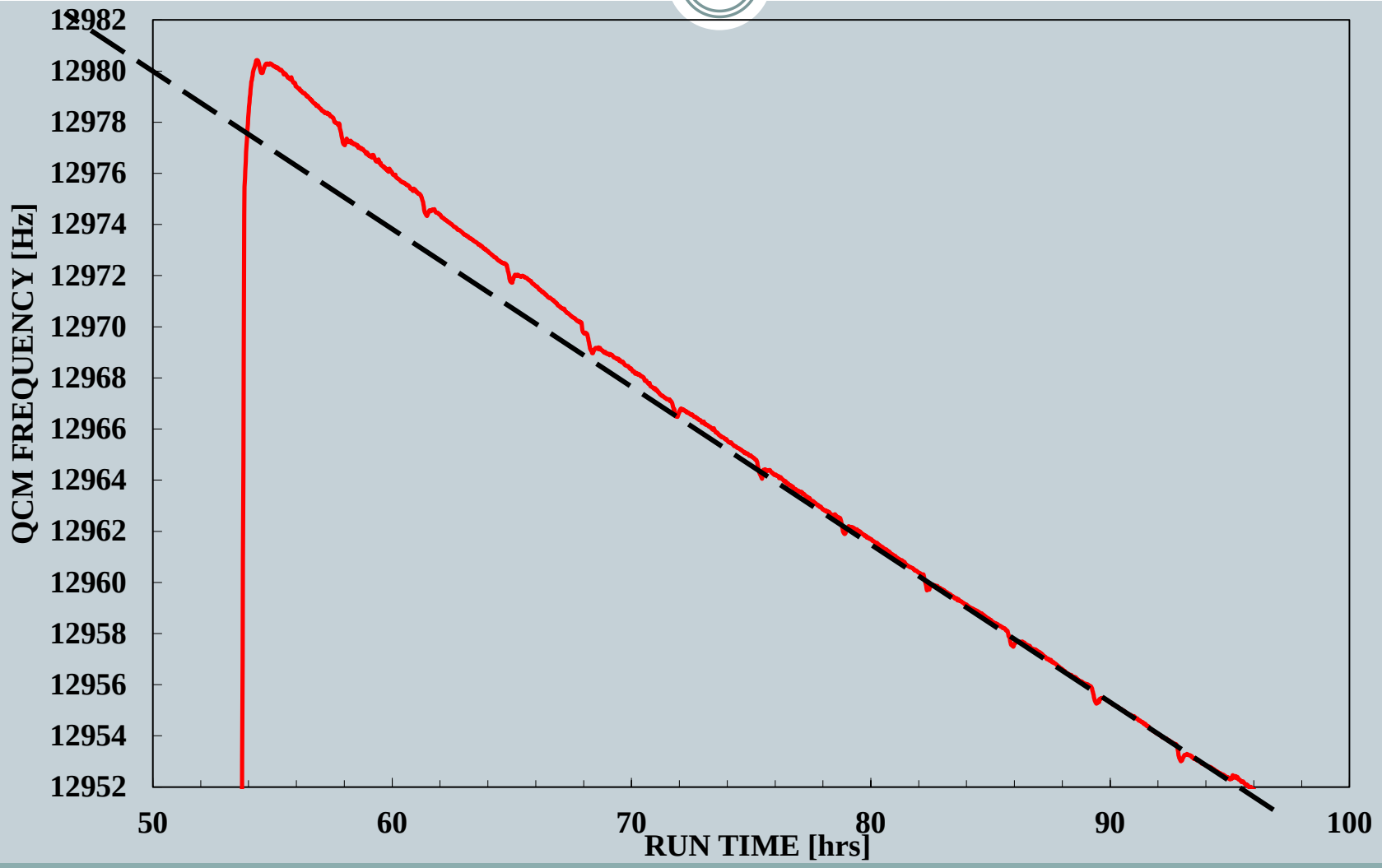
General Test Procedure

- QCM's set to pre-selected temperatures
- Typically begins with thermal stability period (~15-20 hrs.)
 - Empty chamber, collect data on how frequency changes with time
 - Often exhibits variability at or below 0.1 Hz/hr
- Sample weighed, loaded into EC, loading chamber evacuated
- EC travels into test chamber position, warmed to T_{op}
- Sample exposed to test conditions over pre-determined period or when QCM buildup rates have dropped below detectable limits
- Sample returned to loading chamber, chamber repressurized, sample removed and weighed

Desorption Test Procedure

- Select test sample that releases H_2O, not much else
 - From experience, chose G10 fiberglass block, exposed to atmospheric conditions
 - Similar to JWST electronics compartment material
- QCM's collect vapor at various, steady, cryogenic temps.
 - Chose temperatures between 90—140 K
- After sufficient amount of vapor collected, withdraw sample
 - Arbitrary minimum change in frequency ~ 10 kHz
- Continue operating QCM's at constant temperature, record desorption rates every minute over next 1-2 days

Sample Test Run Results (125 K)



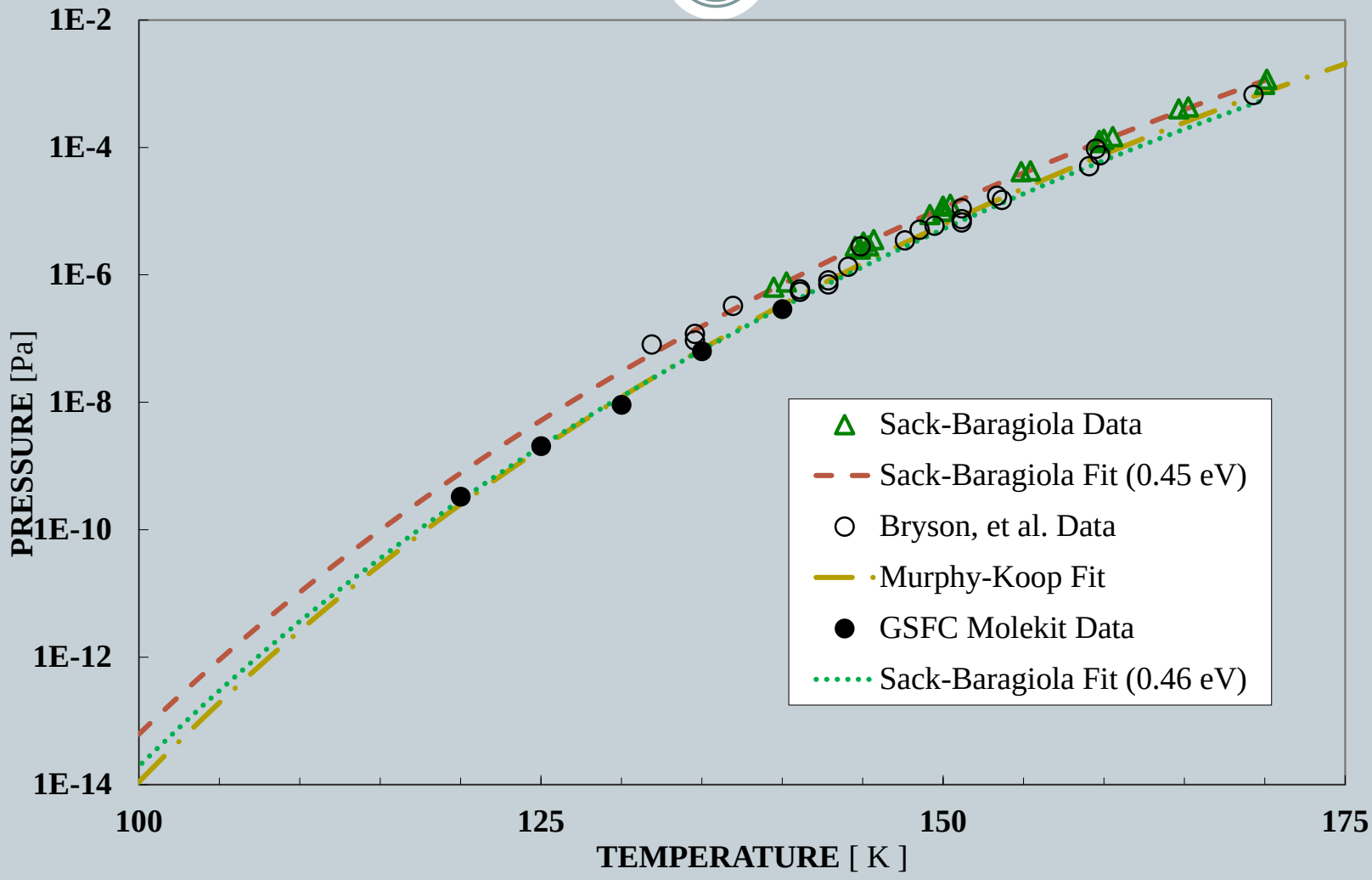
Observation—Phase Change

- Some results exhibited higher initial slopes that relaxed to lower, steady values over time (on order of one day)
 - Similar to behavior recorded by Sack & Baragiola, but rate enhancements were much lower here, less than 2x
 - Identified as solid phase transition to more stable form
 - S-B test runs lasted less than four hours apiece
 - Typically 15 min
 - S-B noted that prior deposition rate factored into amount of amorphous phase desorption rate
 - Uncontrolled in this study

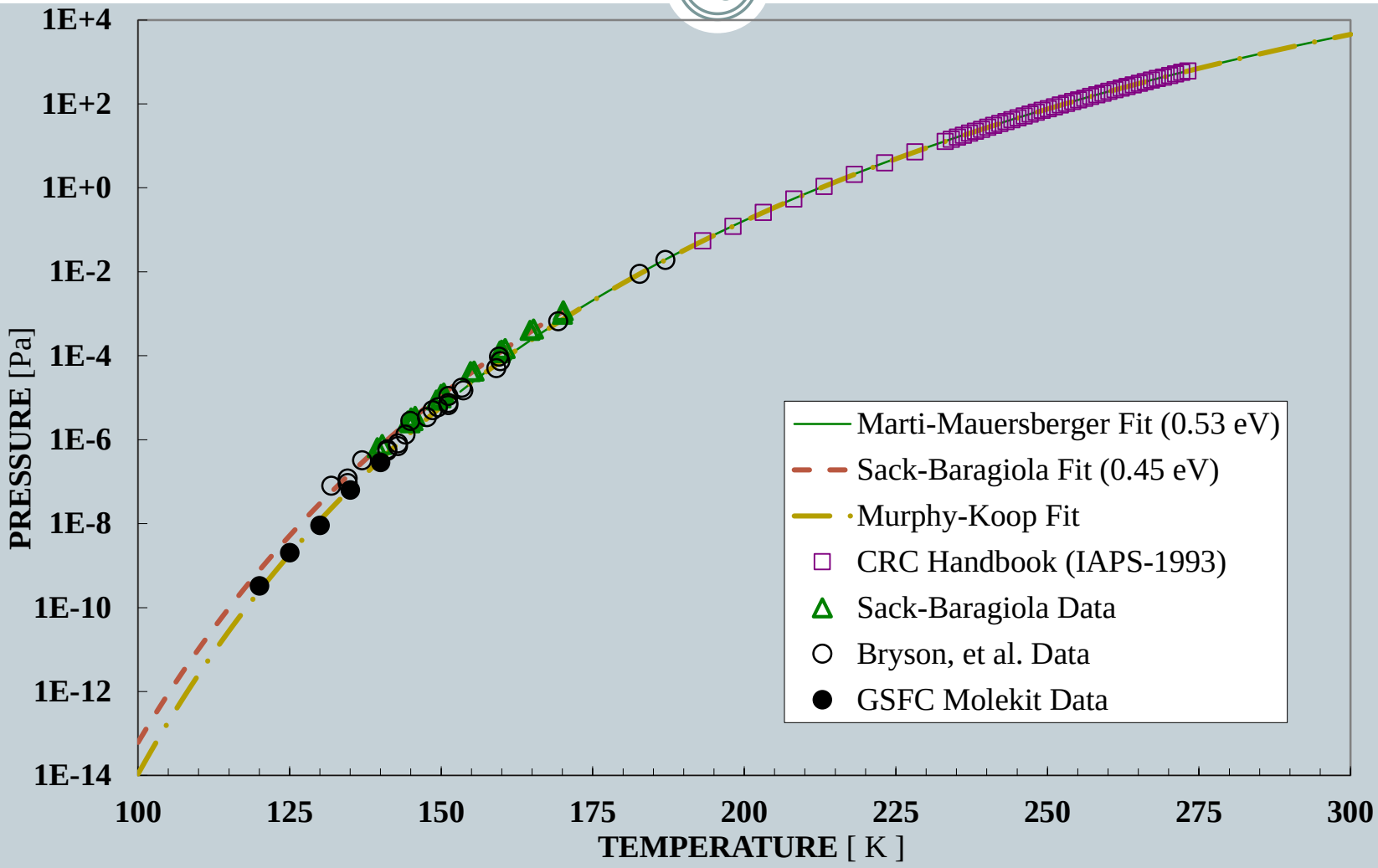
Results

- Performed two runs, attempted to collect data between 120 – 140 K, along with one QCM operating at coldest possible temperature (~90 K)
- Data collected on 90 K demonstrated massive out-of-family behavior, suggests current arrangement would have trouble obtaining useful data below 120 K
 - Could be interference from desorption of H_2O from test chamber walls at 90 K (big area compared to QCM sensor < 1 cm^2)

Model Comparison w/ Test Data



Murphy-Koop Comparison



Concluding Remarks

- Based on comparisons with other investigators, it appears test runs were long enough to firmly establish hexagonal crystalline water vapor desorption rates down to 120 K
- Narrow data set appears to confirm accuracy of Murphy-Koop model formulation
 - Established theoretical basis for form of equation
- JWST project may request further testing to confirm current data